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# Electron paramagnetic resonance study on the *p*-type doping of copper indium disulfide by phosphorus implantation

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High doping efficiencies have been observed in phosphorus-implanted CuInS<sub>2</sub> single crystals by pulsed electron-beam annealing, which could not be achieved by the conventional furnace annealing method. This paper presents the investigations by using the electron paramagnetic resonance measurement on this *p*-type doping effect. The electron paramagnetic resonance signal from the phosphorus interstitials was observed in the as-implanted crystals. The same signal appeared in the subsequently thermally annealed samples but disappeared in the pulsed electron beam annealed ones. This shows the superiority of melting crystal surfaces in the pulsed electron-beam annealing on eliminating the implantation-induced defects to obtain high doping efficiencies.

## I. INTRODUCTION

CuInS<sub>2</sub> single crystal has the potential of being a future optoelectronic material and currently attracts a great deal of attention. However, the *p*-type conductivity control of this material by introducing extrinsic impurities either during the crystal growth or diffusively is a difficult task. The doping efficiency was believed to be limited due to strong compensation effects and the low solubility of usual dopant species.<sup>1</sup> Ion implantation can be adopted to solve the solubility problem but the subsequent annealing is crucial in determining the final electrical property because a large amount of defects are left in the implanted crystals. In the previous work,<sup>1,2</sup> this doping difficulty was overcome by applying phosphorus implantation and pulsed electron beam (PEB) annealing. A hole concentration as high as  $9 \times 10^{19} \text{ cm}^{-3}$  was obtained, which could not be easily achieved by conventional thermal annealing.

The same phenomenon was also observed in CdTe.<sup>3</sup> After phosphorus implantation, most phosphorus elements rest at the interstitial positions and it has been reasoned that, because PEB annealing could effectively eliminate these interstitials while thermal annealing could not, better doping efficiency in the implanted crystals could be obtained by PEB annealing.<sup>3</sup> In this work, in order to confirm our concept, electron paramagnetic resonance (EPR) was used to monitor the implantation induced defects in CuInS<sub>2</sub>, especially the phosphorus interstitials, at the various stages of this doping process.

## II. EXPERIMENT

CuInS<sub>2</sub> single crystals were grown by the traveling heater method (THM)<sup>4</sup> and the chemical vapor transportation method (CVT).<sup>5</sup> After polishing and surface etching, phosphorus implantation was carried out at room temperature, at an incident energy of 100 keV, and at doses between  $10^{13}$  and  $10^{15} \text{ cm}^{-2}$ . In PEB annealing, the electron-beam current ranged between 1 and 60  $\mu\text{A}$  and an approximately 2000-Å-thick Ta<sub>2</sub>O<sub>5</sub> cap was deposited by electron-gun evaporation to prevent the crystal from dissociation during

the annealing. Some of the as-implanted samples were subjected to thermal annealing at 400 °C for one day.

The EPR measurement was performed at room temperature using a Bruker 200D 10/12 system with the microwave frequency in the X band. A sample holder was designed so as to allow the rotation of samples in the cavity. Four kinds of samples (as-grown, P<sup>+</sup>-implanted, P<sup>+</sup>-implanted and thermally annealed, as well as P<sup>+</sup>-implanted and PEB annealed) were subjected to the EPR measurement.

## III. RESULTS AND DISCUSSION

Both the THM and the CVT samples showed similar results. At the as-grown stage, EPR signals over a wide range of the magnetic field were observed in some samples (Fig. 1). From our chemical analysis,<sup>6</sup> the existence of these signals was seen not to depend on the composition of the crystals and thus they were not due to the intrinsic defects in crystals. Transition metals, especially Fe, are major contaminants in the as-grown ternary compounds and their EPR signals have been studied for a long time.<sup>7-10</sup> Our signals were identified as belonging to this category.

At the as-implanted stage, in addition to the signals appearing at the as-grown stage, all the implanted crystals showed a single-line signal as shown in Fig. 2. Since it ap-

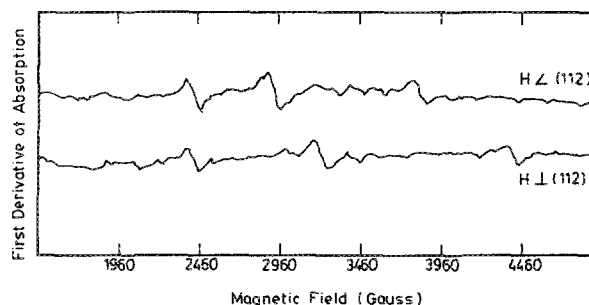


FIG. 1. The EPR signals in the as-grown CuInS<sub>2</sub> single crystal. Upper curve: when the angle between the field and the (112) direction is 45°. Lower curve: when the field is perpendicular to the (112) direction.



FIG. 2. The lower curve shows the EPR signal in the As-P<sup>+</sup>-implanted CuInS<sub>2</sub> single crystal. The upper curve shows the background signal. The frequency is 9.6652 GHz and the gain is  $8 \times 10^5$ .

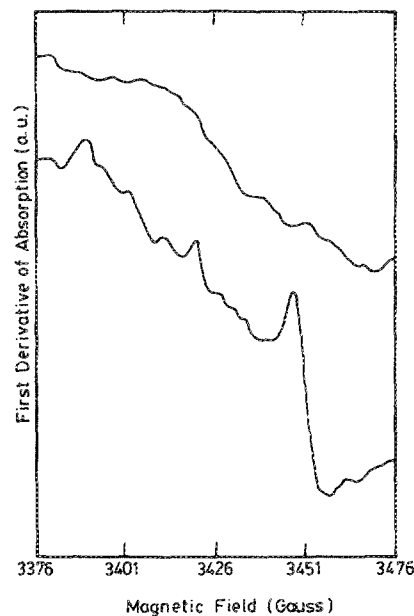


FIG. 3. The EPR signal in the P<sup>+</sup>-implanted and annealed CuInS<sub>2</sub> single crystal. Upper curve: PEB annealed, gain =  $8 \times 10^5$ . Lower curve: thermally annealed, gain =  $1 \times 10^6$ .

peared after the implantation, its correlation with the implantation-induced defects is obvious. With the spectra taken at various orientations, e.g., with the magnetic field rotating in the (112) plane, this signal was seen to be isotropic and its  $g$  value is equal to 2.0011. Its linewidth is only 15 G wide. The extraordinarily narrow linewidth requires exchange effects, and therefore high local defect density, which just corresponds to the characteristics of the implant distribution. The lack of any hyperfine structure indicates that the unpaired electrons do not center at copper, phosphorus, and indium atoms, but rather at sulfur atoms, and the isotropy as well as the  $g$  value indicate  $s$ -orbital characteristics. To be the source of this signal, the sulfur  $4s$  orbital is the most probable candidate. All these could be understood in the following model: After phosphorus implantation, the majority of the implants stop at the interstitials, each of which is surrounded by the four nearest sulfur atoms. Because of the large electronegativity of sulfur atoms, the electrons tend to be attracted away from the copper, indium, and phosphorus atoms to the sulfur atoms during relaxation. Part of the sulfur  $4s$  orbitals are then half-filled due to the extra electrons from phosphorus interstitials and thus give rise to the observed narrow signal. Besides, the coexistence of the signals observed in the as-grown samples at this stage is natural since the ion implantation only affects the near-surface region.

The identification of the signal would be further supported by mapping out the charge distribution of the defect, which is currently under investigation. However, the philosophy of our model has also been successfully applied to the case of CdTe.<sup>11</sup>

As to the annealed stages, the  $g = 2.0011$  signal remained (with a slightly smaller magnitude) in the thermally annealed samples but disappeared in the PEB annealed ones (Fig. 3). This indicates that PEB annealing could effectively

eliminate the phosphorus interstitials but thermal annealing could not, which should strongly affect the final electrical property. This phenomenon could be understood from the characteristics of the two annealings. PEB melts the surface of the crystal to a certain depth and then the surface recrystallizes. Owing to the liquid phase, the phosphorus atoms get the opportunity to occupy sulfur sites during recrystallization and then act as acceptors. On the other hand, the phosphorus interstitials are quite stable during thermal annealing, and thus the interstitial-related signal remains and the corresponding doping efficiency is inferior to that of PEB annealing.

From the above investigations, it is clear that the melting effect of PEB annealing is the key to reach high doping efficiency in phosphorus-implanted CuInS<sub>2</sub> single crystals. It might be reasoned that using ion implantation at high energy and high dose to form an amorphous layer is effective; however, the elimination of implantation-induced defects could also be achieved by thermal annealing, this has not been confirmed and defects still seem restricted to the low implant dose and limited energy applications. Besides, PEB annealing has the additional advantage of being able to perform local annealings.

#### IV. CONCLUSION

The reason why PEB annealing of phosphorus-implanted CuInS<sub>2</sub> single crystals gave better doping efficiency than thermal annealing has been confirmed by the EPR measurements, which show that the ability of melting crystal surfaces makes PEB annealing a favored method for implanted crystals.

## ACKNOWLEDGMENT

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